

# Methanesulfonic Acid Catalyzed Additions to Oleic Acid and Cyclohexene. III. Addition of Acids and Substituted Phenols<sup>1</sup>

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## Abstract

Benzoic acid adds to oleic acid in methanesulfonic acid as catalyst-solvent to form an addition product in 30% yield. Saponification studies on the product reveal that the addition is made via the carboxyl group and no rearrangement of the initial product takes place. A number of substituted benzoic acids were also tried but the yield of addition product was nil. Data are included for the experiments with a number of phenols not previously reported. These include: *o*-chlorophenol, 2,6-di-*tert*-butylphenol, 2,4,6-trichlorophenol, resorcinol, 5-*n*-pentadecylresorcinol, hydroquinone, methyl salicylate, and 3-*n*-pentadecylphenol. Good yields of addition products of cyclohexene are obtained using methanesulfonic acid as catalyst-solvent and the same nucleophiles employed previously.

## Introduction

IN PREVIOUS COMMUNICATIONS from this laboratory (1,2), data were presented showing improvement in yields of products when methanesulfonic acid was used in place of sulfuric acid (3,4) as catalyst-solvent for the addition of phenols and phenyl ethers to oleic acid. Infrared studies of the phenol addition reaction gave support to the theory that the addition proceeds via the formation of an intermediate which subsequently rearranges to give the substituted phenol instead of the phenoxy ether. It was also shown that arylthiols could be added to oleic acid and good yields of product were obtained. The arylthiol addition, however, takes place without subsequent rearrangement of the initial addition product. Invariably, the end product of the reaction was a thioether.

Since diesters have been shown to have considerable utility, it seemed of interest to learn whether the addition reaction could be applied to the addition of aromatic carboxylic acids to oleic acid. If the reaction proceeded so that the addition resulted in the formation of a carbon-carbon bond, then the end product would be a dicarboxylic acid derivative. Some evidence in support of this hypothesis is found in a recent patent (5) and paper (6) describing the preparation and properties of benzoic acid modified alkyd resins. An interesting product was obtained in an attempt to add benzoic acid to oleic acid using methanesulfonic acid as catalyst. Infrared analyses of the product after esterification were inconclusive, in that it was not possible to differentiate between two possible products: methyl benzoxystearate or a carbomethoxyphenyl-stearic acid ester. The former, on saponification followed by esterification with methyl alcohol, would yield a mixture of methyl hydroxystearate and methyl benzoate. If the addition product was a carbomethoxyphenyl-stearic acid derivative, saponification followed by esterification would not

alter the material. Saponification of the benzoic acid addition product yielded hydroxy-stearic acid demonstrating that the addition took place via the carboxyl group and no carbon-carbon bond was formed.

From the addition of benzoic acid to oleic acid there was obtained a 30% yield of molecularly distillable methyl benzoxystearate. Analysis: Calc. C = 74.60, H = 10.11, S.E. = 209. Found C = 75.02, H = 10.37, S.E. = 224. A number of other substituted benzoic acids were tried in the addition reaction. These included: *m*-nitrobenzoic, *p*-nitrobenzoic, *p*-toluic, *o*-chlorobenzoic, *m*-chlorobenzoic, *p*-chlorobenzoic, and anisic acid. Of these, only *m*-nitrobenzoic acid yielded an isolable addition product. However, the analysis of this addition product when compared to theory was poor.

As a possible alternative method for preparing a dicarboxylic acid derivative from oleic acid, the addition of methyl salicylate was tried. It was hoped that methyl salicylate might add via the phenolic hydroxyl group to give an ether intermediate such as that postulated with the addition of phenol. Rearrangement of the intermediate would yield a derivative containing both hydroxyl and carboxyl groups. When the addition reaction with methyl salicylate was carried out at room temperature, the yield of addition product was only 13%. To obtain this yield, the addition of sulfuric acid was required (10–40% of the total acid used), along with the methanesulfonic acid. However, when the addition reaction was run at a temperature between 50–60°C and no sulfuric acid added to the methanesulfonic acid, the yield of methyl salicylate addition product was 53%. Analysis: Calc. C = 72.28, H = 9.89, Sap. No. = 250, OH = 3.79, Mol wt = 448. Found C = 73.28, H = 10.56, Sap. No. = 244, OH = 3.48, Mol wt = 427.

Hydroxyphenylstearic acid derivatives have been shown to have some utility in lubricating grease compositions (7), and also have been reported to have oxidation and rust inhibiting properties in lubricants (8). Because of our continuing interest in lubricants and lubricant additives, and in order to complete the study of phenol additions to oleic acid, this investigation was extended to include a number of phenols which have not been studied previously. Table I summarizes these results.

## Experimental

In general, the additions were carried out in essentially the same manner described in our earlier papers. Illustrative of these experiments is the preparation of the addition product of 2,6-ditertiary-butylphenol and oleic acid, described as follows: To a mixture of 124.9 g of oleic acid (0.442 mole) and 182.3 g of 2,6-ditertiary-butylphenol (0.884 mole), 254.8 g methanesulfonic (2.682 mole) was slowly added with good stirring. As only a slight exotherm was observed, no external cooling was necessary. The addition re-

<sup>1</sup> Presented at the AOCS meeting in Toronto, Canada, 1962.

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quired about 20 min. Stirring was continued for an additional 6 hr after which the reaction mixture was stirred into 3 l of cracked ice and allowed to stand overnight. The organic layer was extracted with ether, and the ether solution freed of acid by washing with 20% aqueous sodium sulfate. The ether extract was dried over anhydrous sodium sulfate and evaporatively distilled. The residue was esterified by adding 500 ml of methanol, 10 g of p-toluenesulfonic acid catalyst, and refluxing the mixture for 16 hr. The reaction mixture was diluted with 2 l of water and extracted with ether. The ether extract, freed of catalyst by water washing, was dried and then stripped of solvent. The residue was subjected to fractional distillation in a molecular still. The early fractions, distilling below 130 C at 5  $\mu$  consisted of excess 2,6-ditertiary-butylphenol and small amounts of methyl oleate. The fraction distilling between 130–170C at 5  $\mu$  (90 g, 40% yield) constituted the substituted methyl stearate.

In a few instances, the recovery of the product required some modification of the above procedure. In the experiments when benzoic acid was added, the excess of benzoic acid was removed, after water washing to remove very soluble methanesulfonic acid, by extracting the ethereal solution with small portions of 1% NaOH. Extraction was continued until the aqueous layer was alkaline. The dilute NaOH solution was allowed to remain in contact with the organic layer for the minimum amount of time (separation of layers in the extraction funnel).

The preferred method for the removal of the excess of phenolic reactant was by fractional distillation. This was done wherever possible. In the preparation of the hydroquinone addition product of oleic acid, a large part of the excess of hydroquinone was removed from the crude reaction product by extracting with hot water. The water washed material was dried, methylene chloride added, and the solution filtered off from the last portions of unreacted hydroquinone.

All of the oleic acid addition products reported in Table I were molecularly distilled.

### Discussion

The yield data for the phenol addition products of oleic acid listed in Table I give additional support for our preference for methanesulfonic acid over sulfuric acid as catalyst-solvent for the addition reaction. In previous work with phenolic substances containing one tertiary butyl group, the yield of addition product when sulfuric acid was used as catalyst ranged from 17.5 (8) to 23% (3). With methanesulfonic acid the yield was more than doubled. In the present work even 2,6-ditertiarybutylphenol was capable of being

added in 40% yield. No addition product was obtained in attempting to add 2,4,6-trichlorophenol or 5-n-pentadecyl resorcinol, but addition products were obtained with o-chlorophenol and resorcinol. The hydroquinone and 2,6-ditertiarybutylphenol addition products of oleic acid may be considered as potential antioxidants. They appear to be less polar than the original phenols, have wider ranges of solubility and would be more compatible in oleaginous media. It is planned to investigate this possibility.

As a further extension of the investigation of methanesulfonic acid catalyzed additions, the addition of nucleophiles to cyclohexene was studied. A number of the substances that were successfully added to oleic acid were used similarly with cyclohexene. The products obtained from the addition of the phenolic nucleophiles were cyclohexyl substituted phenols; the products obtained from the addition of arylthiols were thioethers. In the preparation of the 2-naphthalenethiol addition product of cyclohexene, the excess of thiol was removed by dissolving the crude mixture in a small amount of methylene chloride and precipitating the unchanged 2-naphthalenethiol by the addition of hexane. Phenyl ethers were also capable of being added (See Table II).

Table II shows the yield data for the addition of phenols, phenyl ethers and arylthiols to cyclohexene. The products obtained from these additions are similar to the addition products from oleic acid. Cyclohexyl benzoate was formed by the addition of benzoic acid to cyclohexene. Methyl salicylate added to cyclohexene via the phenolic hydroxyl group. The 66% yield of cyclohexyl resorcinol is another example of the advantages of the methanesulfonic acid catalyst-solvent addition procedure. Bartlett and Garland (9) obtained only a 5% yield of product in condensing cyclohexyl chloride with resorcinol in the presence of aluminum chloride.

Thioanisole is included in Table II to show that thioethers do not add to cyclohexene. This experience is similar to that obtained with oleic acid. It was not unexpected since the end product of thiol additions was thioethers. Anisole and phenetole were successfully added under similar conditions.

The non-oxidizing behavior, and lower tendency to form dark colored side reaction products, was again observed in the above addition reactions using methanesulfonic acid catalyst.

TABLE II  
Cyclohexene Addition Products

Reactant	Yield of Addition Product	Carbon %		Hydrogen %		Hydroxyl %	
		Calc.	Found	Calc.	Found	Calc.	Found
Phenol	44	81.77	81.38	9.15	9.25	9.65	9.45
m-Cresol	62	82.06	82.03	9.54	9.75	8.94	8.70
2-Naphthol	25	84.91	83.90	8.02	7.99	7.52	7.42
o-Chlorophenol	48 <sup>a</sup>	68.40	68.81	7.18	7.24	8.07	7.70
Methyl Salicylate	45 <sup>b</sup>	71.77	71.86	7.74	7.80	7.26	6.60
Resorcinol	66	74.97	74.86	8.39	8.67	Not determined	
2,6-ditert-Butylphenol	50	83.27	83.17	11.18	10.99	Not determined	
p-tert-Butylbenzenethiol	65 <sup>c</sup>	77.35	77.80	9.74	9.97	.....	
2-Naphthalenethiol	21 <sup>d</sup>	79.28	79.21	7.49	7.52	.....	
Anisole	66	82.06	81.86	9.54	9.56	.....	
Phenetole	62	82.30	82.17	9.87	9.90	.....	
Thioanisole	No addition	.....	.....	.....	.....	.....	
Benzoic acid	47 <sup>e</sup>	71.44	72.94	7.90	7.85	.....	

<sup>a</sup> Chlorine %: Calc. 16.83, Found 17.09.

<sup>b</sup> S.E.: Calc. 234, Found 233.

<sup>c</sup> Sulfur %: Calc. 12.91, Found 13.00.

<sup>d</sup> Sulfur %: Calc. 13.23, Found 12.90.

<sup>e</sup> S.E.: Calc. 204, Found 206.

TABLE I  
Methyl Esters of Hydroxyphenylstearic Acids  
 $\text{CH}_3 \cdot (\text{CH}_2)_x \text{CH} \cdot (\text{CH}_2)_y \cdot \text{COOCH}_3$

ROH	Yield of Molecularly Distilled Product	Carbon %		Hydrogen %	
		Calc.	Found	Calc.	Found
2,6-ditert-Butylphenol.....	40 <sup>a</sup>	78.82	78.46	11.63	11.46
o-Chlorophenol.....	36 <sup>b</sup>	70.64	71.64	9.72	10.07
2,4,6-Trichlorophenol.....	No addition	.....	.....	.....	.....
Resorcinol.....	55	73.85	73.67	10.41	10.39
5-n-Pentadecylresorcinol.....	No addition	.....	.....	.....	.....
Hydroquinone.....	40–60	73.85	73.98	10.41	10.36
3-n-Pentadecylphenol.....	33	79.94	80.00	12.08	12.05

<sup>a</sup> Mol wt: Calc. 502, Found 482.

<sup>b</sup> %OH: Calc. 4.0, Found 3.9; %Cl: Calc. 8.34, Found 7.05.

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